

Description

Corrosion inhibitors with improved water solubility and improved film persistence

5

The present invention relates to an additive and to a method of corrosion inhibition on devices for the recovery and transportation of hydrocarbons in crude oil recovery and processing.

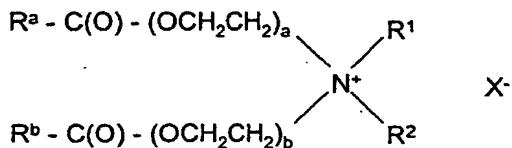
10 In industrial processes where metals come into contact with water or else with oil-water two-phase systems, there is a risk of corrosion. This risk is particularly marked in salt water systems as arise in crude oil production and processing processes. Without special additives for protecting the equipment used, the exploitation of a field and the processing of the crude
15 oil are not possible.

Although such corrosion inhibitors have been known for a long time, they are not optimal in many respects. Many products, e.g. amides/imidazolines from fatty acids and polyamines, are too soluble in oil and are thus present
20 only in a low concentration in the corrosive water phase due to poor partition equilibria (partitioning). Accordingly, these are effective as corrosion inhibitors only to a low degree or only at a high concentration.

DE-A-199 30 683 describes amidamines/imidazolines which are obtained
25 by reacting alkyl polyglycol ether carboxylic acids with polyamines and, due to their structure, have very good water solubility and thus have corrosion protection improved by good partitioning.

Quaternary alkylammonium compounds (quats) represent alternative
30 corrosion inhibitors in the prior art which, as well as the corrosion-inhibiting properties, also have biostatic properties. Despite an improved water solubility, the quats exhibit, for example in comparison to the imidazolines, a significantly reduced film persistence and therefore likewise only lead to effective corrosion protection in a relatively high concentration.
35 Furthermore, the poor biodegradability limits their use in ecologically sensitive fields of application.

US-5 523 433 discloses compounds of the formula



5

in which R^a and R^b may be C₁₂- to C₂₂-alkyl radicals and R¹ and R² may be C₁- to C₄-alkyl radicals. The document discloses the suitability of such compounds as a constituent of fabric softeners.

10 EP-B-0 736 130, EP-B-0 824 631, US-5 648 575 and WO-99/13197 disclose methods of inhibiting gas hydrates using alkoxylated alkylammonium compounds.

US-6 025 302 discloses polyether amine ammonium compounds as gas hydrate inhibitors whose ammonium nitrogen atom carries three alkyl substituents as well as the polyether amine chain.

WO-00/78 706 describes quaternary ammonium compounds but which do not carry carbonyl radicals. The use as corrosion inhibitors is not disclosed.

20

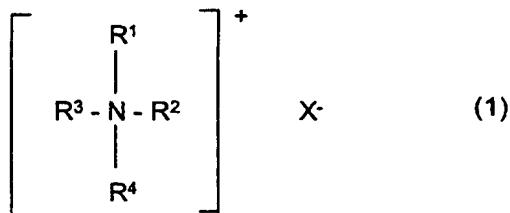
An object of the present invention was thus to find novel corrosion inhibitors which, coupled with consistently good or improved corrosion protection as well as an optimized water solubility, a more rapid film formation and thus improved film persistence, also offer improved biodegradability compared

25 with the corrosion inhibitors of the prior art.

Surprisingly, it has now been found that doubly N-alkoxylated and carbonylated ammonium salts have excellent effectiveness as corrosion inhibitors, and also exhibit improved film persistence and good

30 biodegradability

The invention thus provides for the use of compounds of the formula 1



in which
 $R^1, R^2,$ independently of one another, are radicals of the formulae

5



or

10



R^3 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl

R^4 is an organic radical having 1 to 100 carbon atoms which optionally contains heteroatoms

15 R^5 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl

n is a number from 1 to 20

A is a C₂- to C₄-alkylene group,

B is a C₁- to C₁₀-alkylene group,

C is a C₁- to C₆-alkylene group and

20 X is an anion

as corrosion inhibitors.

The invention further provides a method of inhibiting corrosion at metal

25 surfaces, in particular of iron-containing metals, by adding at least one compound of the formula 1 to a corrosive system which is in contact with the metal surfaces.

The invention further provides the compounds of the formula (1), but where

those compounds in which R^4 does not contain a heteroatom and R^1 and R^2 simultaneously have the meaning given in formula (2) are excluded.

For the purposes of this invention, corrosive systems are preferably liquid/liquid or liquid/gaseous multiphase systems consisting of water and

hydrocarbons which contain, in free and/or dissolved form, corrosive constituents, such as salts and acids. The corrosive constituents can also be gaseous, such as, for example, hydrogen sulfide and carbon dioxide. For the purposes of this invention, hydrocarbons are organic compounds 5 which are constituents of crude oil/natural gas, and secondary products thereof.

A can be straight-chain or branched and is preferably an ethylene or propylene group, in particular an ethylene group. The alkoxy groups 10 referred to by (A-O)_n can also be mixed alkoxy groups.

B can be straight-chain or branched and is preferably a C₂- to C₄-alkylene group, in particular an ethylene or propylene group.

15 C can be straight-chain or branched and is preferably a C₂- to C₄-alkylene group, in particular a methylene or ethylene group.

n is preferably a number between 2 and 6.

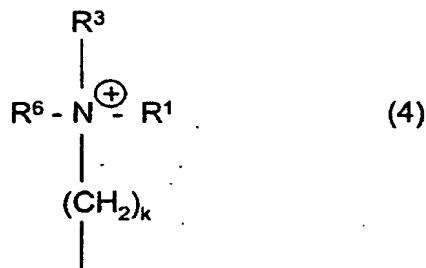
20 R⁵ is preferably an alkyl or alkenyl group having 2 to 24 carbon atoms, in particular 4 to 12 carbon atoms.

R³ is preferably an alkyl or alkenyl group from 2 to 12 carbon atoms, in 25 particular those groups having 4 to 8 carbon atoms and specifically butyl groups.

R⁴ can be any organic radical which contains 1 to 100 carbon atoms and which can contain heteroatoms. If R⁴ contains heteroatoms, then these are 30 preferably nitrogen or oxygen atoms or both, preferably both. The nitrogen atoms can be in quaternized form.

In a further preferred embodiment, R⁴ comprises 1 to 20 alkoxy groups derived from C₂- to C₄-alkylene oxide, in particular from ethylene oxide and/or propylene oxide. In particular, R⁴ can be a radical according to 35 formula (2) or (3).

In a particularly preferred embodiment, R⁴ corresponds to a radical of the formula (4)



where the bonding to the nitrogen atom in formula 1 takes place by the free
 5 valence of the $(\text{CH}_2)_k$ group. In formula (4), R^6 is a radical of the formulae



or

10

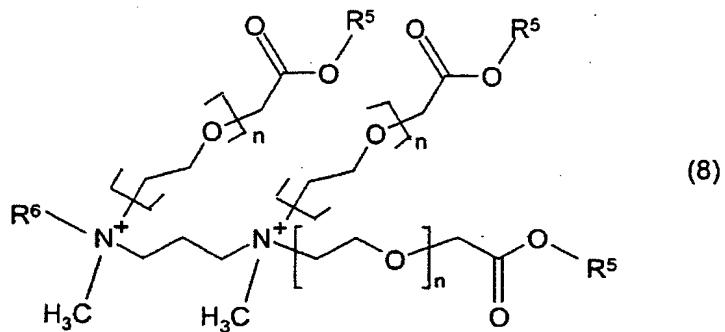
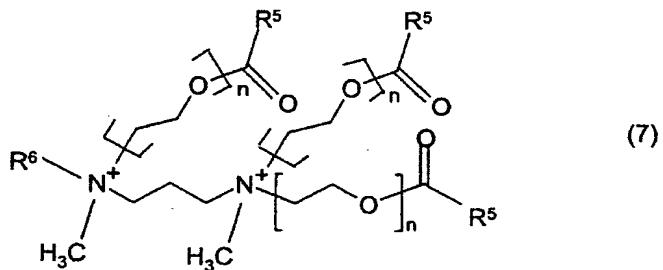
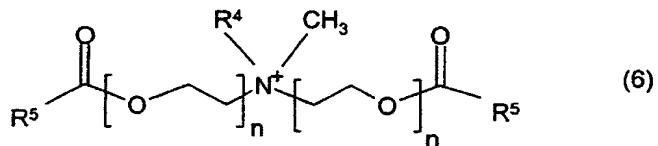
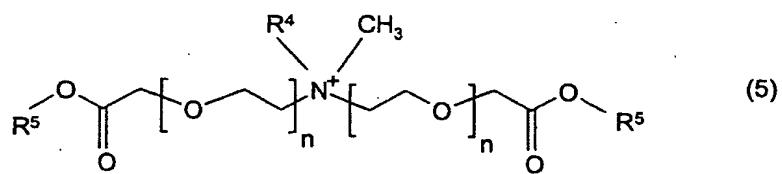


or C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl, in each case with the preferred
 ranges given above for A, B, n, R³ and R⁵. k is 2 or 3, R¹ and R³ have the
 15 meanings given above.

Suitable counterions X are all ions which do not impair the solubility of the
 compounds of the formula (1) in the corrosive organic-aqueous mixed
 phases. Such counterions are, for example, methylsulfate ions
 20 (methosulfate) or halide ions.

Particularly preferred compounds (shown without counterions) correspond
 to the formulae (5) to (8)

6



5 The compounds according to the invention can be used on their own or in combination with other known corrosion inhibitors. In general, the amount of corrosion inhibitor according to the invention used is sufficient to provide adequate corrosion protection under the given conditions. Preferred use concentrations, based on the pure compounds according to the invention,
 10 are 5 to 5000 ppm, preferably 10 to 1000, in particular 15 to 150 ppm.

Particularly suitable corrosion inhibitors are also mixtures of the products according to the invention with other corrosion inhibitors known from the literature, such as amide amines and/or imidazolines from fatty acids and

polyamines and salts thereof, quaternary ammonium salts, oxyethylated/oxypropylated amines, amphoglycinates and amphotropionates, betaines or compounds described in DE-A-19 930 683.

- 5 The compounds according to the invention can be prepared by reacting alkoxylated alkylamines or alkylaminoalkyleneamines with monochloro-carboxylic acids to give the corresponding ether carboxylic acids and subsequent esterification with alkanols. On the other hand, the bisalkoxylated monoalkylamines or alkylaminoalkyleneamines can be reacted directly with carboxylic acids and derivatives thereof, such as anhydrides, carbonyl chlorides or esters thereof, to give the esters according to the invention. The quaternization is then carried out with suitable alkylating agents.
- 10
- 15 The preparation of alkoxylated alkylamines or alkylaminoalkyleneamines is described in the prior art.

The basis of the alkoxylated alkylamines used are alkylamines having C₁-to C₃₀-alkyl radicals or C₂- to C₃₀-alkenyl radicals, preferably C₃- to C₈-alkylamines. Suitable alkylamines are, for example, n-butylamine, isobutylamine, pentylamine, hexylamine, octylamine, cyclopentylamine, cyclohexylamine.

The basis of the alkoxylated alkylaminoalkyleneamines used are aminoalkyleneamines having C₁- to C₃₀-alkyl radicals or C₂- to C₃₀-alkenyl radicals and k = 2 or 3. Suitable aminoalkyleneamines are, for example, fatty alkylpropylenediamines, such as tallow fatty propylenediamine, stearylpropylenediamine, oleylpropylenediamine, laurylpropylenediamine, dodecylpropylenediamine and octylpropylenediamine.

30 The alkylamines or alkylaminoalkyleneamines are generally reacted with ethylene oxide, propylene oxide, butylene oxide or mixtures of different such alkylene oxides, where ethylene oxide or mixtures of ethylene oxide and propylene oxide are preferred. Based on alkylamine or alkylaminoalkyleneamines, 1-40 mol of alkylene oxide are supplied, preferably 1-12 mol.

The alkoxylation takes place without a diluent, but can also be carried out in solution. Suitable solvents for the alkoxylation are inert ethers, such as dioxane, tetrahydrofuran, glyme, diglyme and MPEGs.

- 5 In general, the alkoxylation in the first reaction step is carried out uncatalyzed up to > 95% by weight of tert-nitrogen. Higher alkoxylation takes place following the addition of basic compounds as catalysts. Basic compounds which can be used are alkaline earth metal/alkali metal hydroxides or alkoxides (sodium methoxide, sodium ethoxide, potassium 10 tert-butoxide), but preference is given to alkali metal hydroxides, particularly sodium hydroxide or potassium hydroxide.

For the preparation of the compounds according to the invention, in a subsequent reaction step the amine-oxyethylate mixtures are reacted with 15 a chlorocarboxylic acid derivative and a base, preferably dry sodium chloroacetate and sodium hydroxide. This may involve reacting the oxyethylate mixture with 100 to 150 mol% of sodium chloroacetate at 30 to 100°C and, simultaneously or subsequently, adding solid sodium hydroxide or potassium hydroxide, so that the sum of the base already present in the 20 oxyethylate mixture and the amount of base additionally added corresponds to the amount of sodium chloroacetate. The amount of base already present from the reaction with the alkylene oxide can thus be utilized directly for the subsequent Williamson synthesis and does not, as in the synthesis of a standard oxyethylate, have to be washed out.

25 Subsequently to the alkylation reaction, the alkoxylated amine ether carboxylic acid alkali metal salts are converted into the free ether carboxylic acid. For this purpose, the mixture is acidified to pH < 3 with a strong mineral acid (hydrochloric acid, sulfuric acid) and the ether carboxylic acid 30 is separated off as the upper phase while hot by phase separation above its cloud point.

The subsequent esterification of the alkoxylated amine ether carboxylic acids generally takes place by direct reaction of the free acid with 35 corresponding alcohols at temperatures of 100-200°C, where the water of reaction is removed by distillation. The esterification can be accelerated by adding suitable acidic catalysts with a pK_a value of less than or equal to 5

or by removing the water of reaction azeotropically using suitable solvents. Suitable catalysts are, for example, sulfonic acid and alkylstannic acids.

For the esterification of the alkoxylated amine ether carboxylic acids, use is made of alcohols having C₄- to C₃₀-alkyl radicals or C₄- to C₃₀-alkenyl radicals, preferably fatty alcohols. Suitable alcohols are, for example, 2-ethylhexanol, octanol, decanol, lauryl alcohol, palmityl alcohol, stearyl alcohol and oleyl alcohol.

The compounds according to the invention can also be prepared by esterification of the amine/oxyethylate mixtures with carboxylic acids and derivatives thereof, such as carbonyl chlorides, carboxylic anhydrides and carboxylic acid esters. The esterification with free carboxylic acids takes place at temperatures of 100-200°C, where the water of reaction is removed by distillation. The esterification can be accelerated by adding suitable acidic catalysts with a pK_a value of less than or equal to 5 or by removing the water of reaction azeotropically using suitable solvents. Suitable carboxylic acids are acetic acid, propionic acid, caproic acid, caprylic acid, 2-ethylhexanoic acid and fatty acids or anhydrides thereof, methyl esters and chlorides.

The preparation of the compounds according to the invention then takes place by quaternization of the tertiary nitrogen atoms with a suitable alkylating agent at 50 to 150°C. Suitable alkylating agents are alkyl halides and alkyl sulfates, preferably methylene chloride, butyl bromide and dimethyl sulfate.

Examples:

a) General procedure for the preparation of alkoxylated amine ether carboxylic acids

2 mol of the corresponding alkoxylated amine or 1 mol of the corresponding alkoxylated diamine (according to OH number) were initially introduced into a stirred apparatus under nitrogen blanketing and heated to 40°C. Then, 650 g (4.8 mol) of sodium chloroacetate were introduced for alkoxylated monoamines, or 488 g (3.6 mol) of sodium chloroacetate were introduced for alkoxylated diamines, and the reaction mixture was heated to 50°C.

After 30 min in each case, 192 g (4.8 mol) or 144 g (3.6 mol) of NaOH microprills were added in 6 portions such that the temperature does not exceed 55°C. The mixture was after-reacted for 2 h at 70°C. 10% strength hydrochloric acid was then metered in until a pH < 3 was reached. The 5 mixture was then heated to 95°C and transferred to a heatable stirred apparatus with bottom drain outlet. Phase separation was carried out after 15 min at 105-108°C. The aqueous lower phase was discarded. With products which cannot be separated by heating to above the cloud point, the water of reaction was removed by distillation and the salt which 10 precipitated out was filtered off.

Example 1 (n-butylamine + 6 EO-ECA)

699 g of n-butylamine + 6 EO (OH number: 321.1 mg of KOH/g) gave 970 g of n-butylamine + 6 EO-ECA with AN = 221.5 mg of KOH/g 15 (corresponds to 91.9% conversion) and bas.-N = 3.00%.

Example 2 (caprylamine + 6 EO-ECA)

801 g of caprylamine + 6 EO (OH number: 280.1 mg of KOH/g) gave 1045 g of caprylamine + 6 EO-ECA with AN = 200.9 mg of KOH/g 20 (corresponds to 92.5% conversion) and bas.-N = 2.69%.

Example 3 (caprylamine + 10 EO-ECA)

1147 g of caprylamine + 10 EO (OH number: 195.7 mg of KOH/g) gave 1412 g of caprylamine + 10 EO-ECA with AN = 144.9 mg of KOH/g 25 (corresponds to 89.0% conversion) and bas.-N=1.90%.

Example 4 (tallow fatty propylenediamine + 10 EO-ECA)

768 g of tallow fatty propylenediamine + 10 EO (OH number: 219.2 mg of KOH/g) gave 970 g of tallow fatty propylenediamine + 10 EO-ECA with AN 30 = 156.7 mg of KOH/g (corresponds to 87.7% conversion) and bas.-N = 2.88%.

Example 5 (tallow fatty propylenediamine + 25 EO-ECA)

1316 g of tallow fatty propylenediamine + 25 EO (OH number: 127.9 mg of KOH/g) gave 1700 g of tallow fatty propylenediamine + 25 EO-ECA with 35 AN = 85.0 mg of KOH/g (corresponds to 84.0% conversion) and bas.-N = 1.49%.

Example 6 (tallow fatty propylenediamine + 30 EO-ECA)

1699 g of tallow fatty propylenediamine + 30 EO (OH number: 99.1 mg of KOH/g) gave 2043 g of tallow fatty propylenediamine + 30 EO-ECA with AN = 66.5 mg of KOH/g (corresponds to 80.9% conversion) and bas.-N =

5 1.30%.

Example 7 (tallow fatty propylenediamine + 35 EO-ECA)

1919 g of tallow fatty propylenediamine + 35 EO (OH number: 87.7 mg of KOH/g) gave 2301 g of tallow fatty propylenediamine + 35 EO-ECA with

10 AN = 63.2 mg of KOH/g (corresponds to 85.5% conversion) and bas.-N = 1.19%.

Example 8 (laurylpropylenediamine + 10 EO-ECA)

673 g of laurylpropylenediamine + 10 EO (OH number: 250.0 mg of KOH/g)

15 gave 1071 g of laurylpropylenediamine + 10 EO-ECA with AN = 149.2 mg of KOH/g (corresponds to 90.5% conversion) and bas.-N = 2.54%.

Example 9 (laurylpropylenediamine + 30 EO-ECA)

1639 g of laurylpropylenediamine + 30 EO (OH number: 102.7 mg of KOH/g)

20 gave 1964 g of laurylpropylenediamine + 30 EO-ECA with AN = 82.3 mg of KOH/g (corresponds to 97.1% conversion) and bas.-N = 1.40%.

b) General procedure for the preparation of alkoxylated amine ether carboxylic acid alkyl esters

25

1 mol or 0.5 mol (according to AN) of the corresponding alkoxylated alkylamineether carboxylic acid or alkylene diamineether carboxylic acid, respectively, were initially introduced into a stirred apparatus with nitrogen blanketing and an excess (about 1.5 mol equivalents per carboxylic acid function) of alcohol was added. Following the addition of 0.5% by weight of FASCAT 4100 (butylstannic acid), the mixture was heated to 100°C to

30 180°C, during which the water of reaction distilled off. After a reaction time of 8 h or after an acid number of AN < 5 mg of KOH/g had been reached, the reaction was complete and excess alcohol and residual water were 35 removed by distillation under reduced pressure.

Example 10 (n-butylamine + 6 EO 2-ethylhexyl ECA ester)

507 g of n-butylamine + 6 EO-ECA and 391 g of 2-ethylhexanol gave 707 g of n-butylamine + 6 EO 2-ethylhexyl ECA ester with AN = 4.1 mg of KOH/g and VN = 158.1 mg of KOH/g (corresponds to 97.4% conversion).

5 Example 11 (caprylamine + 6 EO 2-ethylhexyl ECA ester)
559 g of caprylamine + 6 EO-ECA and 391 g of 2-ethylhexanol gave 738 g of caprylamine + 6 EO 2-ethylhexyl ECA ester with AN = 3.3 mg of KOH/g and VN = 147.0 mg of KOH/g (corresponds to 97.8% conversion).

10 Example 12 (caprylamine + 10 EO 2-ethylhexyl ECA ester)
774 g of caprylamine + 10 EO-ECA and 391 g of 2-ethylhexanol gave 999 g of caprylamine + 10 EO 2-ethylhexyl ECA ester with AN = 4.8 mg of KOH/g and VN = 114.1 mg of KOH/g (corresponds to 95.8% conversion).

15 Example 13 (tallow fatty propylenediamine + 10 EO 2-ethylhexyl ECA ester)
537 g of tallow fatty propylenediamine + 10 EO-ECA and 293 g of 2-ethylhexanol gave 688 g of tallow fatty propylenediamine + 10 EO 2-ethylhexyl ECA ester with AN = 4.7 mg of KOH/g and VN = 121.3 mg of KOH/g
20 (corresponds to 96.1% conversion).

Example 14 (tallow fatty propylenediamine + 25 EO ethylhexyl ECA ester)
990 g of tallow fatty propylenediamine + 25 EO-ECA and 293 g of 2-ethylhexanol gave 1068 g of tallow fatty propylenediamine + 25 EO 2-ethylhexyl ECA ester with AN = 6.7 mg of KOH/g and VN = 74.6 mg of KOH/g
25 (corresponds to 91.0% conversion).

Example 15 (tallow fatty propylenediamine + 30 EO ethylhexyl ECA ester)
1266 g of tallow fatty propylenediamine + 30 EO-ECA and 293 g of 2-ethylhexanol gave 1374 g of tallow fatty propylenediamine + 30 EO 2-ethylhexyl ECA ester with AN = 3.5 mg of KOH/g and VN = 61.7 mg of KOH/g
30 (corresponds to 94.3% conversion).

Example 16 (tallow fatty propylenediamine + 35 EO dodecyl ECA ester)
1332 g of tallow fatty propylenediamine + 35 EO-ECA and 419 g of lauryl alcohol gave 1523 g of tallow fatty propylenediamine + 35 EO 2-dodecyl ECA ester with AN = 4.9 mg of KOH/g and VN = 54.2 mg of KOH/g
35 (corresponds to 90.9% conversion).

Example 17 (laurylpropylenediamine + 10 EO 2-ethylhexyl ECA ester)
564 g of laurylpropylenediamine + 10 EO-ECA and 293 g of 2-ethylhexanol gave 703 g of laurylpropylenediamine + 10 EO 2-ethylhexyl ECA ester with AN = 3.6 mg of KOH/g and VN = 117.9 mg of KOH/g (corresponds to

5 96.9% conversion).

Example 18 (laurylpropylenediamine + 30 EO dodecyl ECA ester)

1023 g of laurylpropylenediamine + 30 EO-ECA and 419 g of lauryl alcohol gave 1213 g of laurylpropylenediamine + 30 EO dodecyl ECA ester with

10 AN = 6.0 mg of KOH/g and VN = 66.8 mg of KOH/g (corresponds to 91.0% conversion).

c) General procedure for the preparation of alkoxylated aminecarboxylic acid esters by reaction with carboxylic acids

15

1 mol or 0.5 mol (according to OH number) of the corresponding alkoxylated alkylamine or alkylene diamine, respectively, was initially introduced into a stirred apparatus with nitrogen blanketing, and 1 mol equivalent (depending on OH function) of the corresponding carboxylic acid 20 was added (depending on OH function). Following the addition of 0.5% by weight of FASCAT 4100 (butylstannic acid), the mixture was heated to 100°C to 200°C, during which the water of reaction distilled off. After a reaction time of 8 h or after an acid number of AN < 10 mg of KOH/g had been reached, the reaction was complete and residual water was removed 25 by distillation under reduced pressure.

d) General procedure for the preparation of alkoxylated aminecarboxylic acid esters by reaction with carboxylic anhydrides

30

1 mol or 0.5 mol (according to OH number) of the corresponding alkoxylated alkylamine or alkylene diamine, respectively, was initially introduced into a stirred apparatus under nitrogen blanketing, and 1 mol equivalent of the corresponding carboxylic anhydride (depending on OH function) was added. The mixture was heated to 100°C to 150°C. After a 35 reaction time of 8 h at this reaction temperature, the liberated carboxylic acid was distilled off.

Example 19 (n-butylamine + 6 EO acetic acid ester)

349 g of n-butylamine + 6 EO (OH number: 321.1 mg of KOH/g) and 204 g of acetic anhydride gave 434 g of n-butylamine + 6 EO acetic acid ester with AN = 0.1 mg of KOH/g and VN = 260.2 mg of KOH/g.

5 Example 20 (n-butylamine + 6 EO propionic acid ester)

349 g of n-butylamine + 6 EO (OH number: 321.1 mg of KOH/g) and 260 g of propionic anhydride gave 465 g of n-butylamine + 6 EO propionic acid ester with AN = 0.7 mg of KOH/g and VN = 244.9 mg of KOH/g.

10 Example 21 (n-butylamine + 6 EO 2-ethylhexanoic acid ester)

349 g of n-butylamine + 6 EO (OH number: 321.1 mg of KOH/g) and 288 g of 2-ethylhexanoic acid gave 594 g of n-butylamine + 6 EO 2-ethylhexanoic acid ester with AN = 6.4 mg of KOH/g and VN = 191.8 mg of KOH/g.

15 Example 22 (n-butylamine + 6 EO isononanoic acid ester)

349 g of n-butylamine + 6 EO (OH number: 321.1 mg of KOH/g) and 316.5 g of isononanoic acid gave 636 g of n-butylamine + 6 EO isononanoic acid ester with AN = 5.9 mg of KOH/g and VN = 183.3 mg of KOH/g.

20

Example 23 (caprylamine + 6 EO acetic acid ester)

401 g of caprylamine + 6 EO (OH number: 280.1 mg of KOH/g) and 204 g of acetic anhydride gave 484 g of caprylamine + 6 EO acetic acid ester with AN = 0.2 mg of KOH/g and VN = 231.5 mg of KOH/g.

25

Example 24 (caprylamine + 6 EO propionic acid ester)

401 g of caprylamine + 6 EO (OH number: 280.1 mg of KOH/g) and 260 g of propionic anhydride gave 517 g of caprylamine + 6 EO propionic acid ester with AN = 0.4 mg of KOH/g and VN = 220.8 mg of KOH/g.

30

Example 25 (caprylamine + 6 EO 2-ethylhexanoic acid ester)

401 g of caprylamine + 6 EO (OH number: 280.1 mg of KOH/g) and 288 g of 2-ethylhexanoic acid gave 643 g of caprylamine + 6 EO 2-ethylhexanoic acid ester with AN = 8.1 mg of KOH/g and VN = 179.6 mg of KOH/g.

35

Example 26 (caprylamine + 6 EO isononanoic acid ester)

401 g of caprylamine + 6 EO (OH number: 280.1 mg of KOH/g) and 316.5 g of isononanoic acid gave 672 g of caprylamine + 6 EO isononanoic acid ester with AN = 4.1 mg of KOH/g and VN = 167.2 mg of KOH/g.

5 Example 27 (tallow fatty propylenediamine + 25 EO propionic acid ester)
658 g of tallow fatty propylenediamine + 25 EO (OH number: 127.9 mg of KOH/g) and 195 g of propionic anhydride gave 750 g of tallow fatty propylenediamine + 25 EO propionic acid ester with AN = 0.7 mg of KOH/g and VN = 114.3 mg of KOH/g.

10 Example 28 (tallow fatty propylenediamine + 25 EO 2-ethylhexanoic acid ester)
658 g of tallow fatty propylenediamine + 25 EO (OH number: 127.9 mg of KOH/g) and 216 g of 2-ethylhexanoic acid gave 859 g of tallow fatty propylenediamine + 25 EO 2-ethylhexanoic acid ester with AN = 8.6 mg of KOH/g and VN = 107.6 mg of KOH/g.

15 Example 29 (tallow fatty propylenediamine + 25 EO coconut fatty acid ester)
20 658 g of tallow fatty propylenediamine + 25 EO (OH number: 127.9 mg of KOH/g) and 310 g of coconut fatty acid (AN = 271.3 mg of KOH/g) gave 951 g of tallow fatty propylenediamine + 25 EO coconut fatty acid ester with AN = 4.5 mg of OH/g and VN = 93.9 mg of KOH/g.

25 Example 30 (laurylpropylenediamine + 30 EO coconut fatty acid ester)
820 g of laurylpropylenediamine + 30 EO (OH number: 102.7 mg of KOH/g) and 310 g of coconut fatty acid (AN = 271.3 mg of KOH/g) gave 1107 g of laurylpropylenediamine + 30 EO coconut fatty acid ester with AN = 3.6 mg of KOH/g and VN = 79.9 mg of KOH/g.

30 e) General procedure for the quaternization of the alkoxyated amine ether carboxylic acid alkyl esters or the alkoxyated aminecarboxylic acid esters
35 0.5 mol (according to VN number) of the corresponding alkoxyated amine ether carboxylic acid alkyl ester or of the alkoxyated aminecarboxylic acid ester was initially introduced into a stirred apparatus with nitrogen blanketing and heated to 60°C. 0.4 mol of dimethyl sulfate was added dropwise to this such that the reaction temperature did not exceed 80-

90°C. The reaction mixture was then after-stirred for 3 h at 90°C. After this procedure, the compounds, described by examples 10 to 30, were quaternized (examples 31 to 51, as listed in table 1 and 2).

5 Effectiveness of the compounds according to the invention as corrosion inhibitors

The compounds according to the invention were tested as corrosion inhibitors in the Shell wheel test. Coupons made of C-steel (DIN 1.1203 10 with a surface area of 15 cm²) were dipped into a saltwater/petroleum mixture (9:1.5% strength NaCl solution adjusted to pH 3.5 with acetic acid) and exposed to this medium at a circulatory rate of 40 rpm at 70°C for 24 hours. The concentration of the inhibitor was 50 ppm of a 40% solution of 15 the inhibitor. The protection values were calculated from the mass decrease of the coupons, based on a blank value.

In the tables below, "comparison" refers to a residue amine-quat based on dicocoalkyldimethylammonium chloride (corrosion inhibitor of the prior art).

20 Table 1: (SHELL wheel test)

| Example | Corrosion inhibitor | Ø Protection % |
|------------|----------------------|----------------|
| Comparison | | 36.0 |
| 31 | Quat from example 10 | 86.0 |
| 32 | Quat from example 11 | 88.6 |
| 33 | Quat from example 12 | 79.2 |
| 34 | Quat from example 13 | 65.3 |
| 35 | Quat from example 14 | 51.8 |
| 36 | Quat from example 15 | 47.7 |
| 37 | Quat from example 16 | 76.3 |
| 38 | Quat from example 17 | 64.0 |
| 39 | Quat from example 18 | 81.9 |
| 40 | Quat from example 19 | 32.4 |
| 41 | Quat from example 20 | 32.8 |
| 42 | Quat from example 21 | 86.0 |
| 43 | Quat from example 22 | 85.0 |
| 44 | Quat from example 23 | 49.9 |

| | | |
|----|----------------------|------|
| 45 | Quat from example 24 | 52.3 |
| 46 | Quat from example 25 | 87.1 |
| 47 | Quat from example 26 | 90.4 |
| 48 | Quat from example 27 | 35.2 |
| 49 | Quat from example 28 | 37.1 |
| 50 | Quat from example 29 | 89.6 |
| 51 | Quat from example 30 | 84.6 |

The products were also tested in the LPR test (test conditions analogous to ASTM D 2776).

5 Table 2: (LPR test)

| Example | Corrosion inhibitor | Protection after [%] | | |
|------------|---------------------|----------------------|--------|--------|
| | | 10 min | 30 min | 60 min |
| Comparison | | 53.9 | 61.2 | 73.7 |
| 52 | Example 31 | 74.3 | 84.8 | 87.0 |
| 53 | Example 32 | 78.4 | 86.1 | 92.3 |
| 54 | Example 33 | 70.2 | 74.7 | 81.0 |
| 55 | Example 37 | 51.9 | 65.6 | 74.9 |
| 56 | Example 39 | 53.5 | 65.9 | 75.2 |
| 57 | Example 42 | 67.7 | 75.6 | 79.0 |
| 58 | Example 43 | 76.1 | 83.6 | 86.7 |
| 59 | Example 46 | 78.0 | 85.7 | 87.9 |
| 60 | Example 47 | 80.2 | 87.2 | 93.4 |
| 61 | Example 50 | 53.9 | 67.1 | 78.6 |
| 62 | Example 51 | 78.0 | 85.7 | 87.9 |

As can be seen from the above test results, the products according to the invention have very good corrosion protection properties at a low concentration. The compounds are biodegradable, as shown below.

10

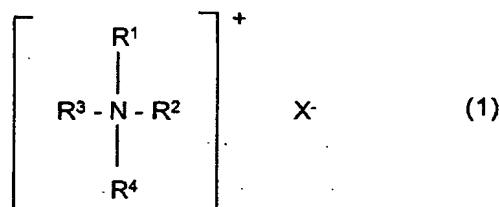
Table 3: (Storm test in accordance with OECD 301 B)

| Example | Corrosion inhibitor | Biodegradability in % |
|------------|---------------------|-----------------------|
| Comparison | | 28 |
| 63 | Example 32 | 46 |
| 64 | Example 46 | 52 |
| 65 | Example 47 | 38 |

| | | |
|-----------|-------------------|-----------|
| 66 | Example 51 | 55 |
|-----------|-------------------|-----------|

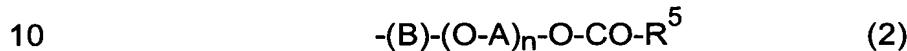
Claims

1. The use of compounds of the formula 1



5

in which
 R^1, R^2 , independently of one another, are radicals of the formulae



or



15

R^3 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl

R^4 is an organic radical having 1 to 100 carbon atoms which optionally contains heteroatoms

R^5 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl

20 n is a number from 1 to 20

A is a C₂- to C₄-alkylene group,

B is a C₁- to C₁₀-alkylene group,

C is a C₁- to C₆-alkylene group and

X is an anion

25 as corrosion inhibitors.

2. The use as claimed in claim 1, in which A is an ethylene or propylene group.

30 3. The use as claimed in claim 1 and/or 2, in which B is a C₂- to C₄-alkylene group.

4. The use as claimed in one or more of claims 1 to 3, in which C is a C₂- to C₄-alkylene group.

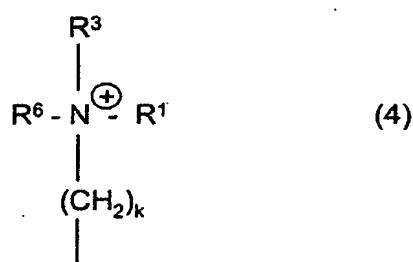
5. The use as claimed in one or more of claims 1 to 4, in which n is a number between 2 and 6.

6. The use as claimed in one or more of claims 1 to 5, in which R⁵ is an alkyl or alkenyl group having 2 to 24 carbon atoms.

10 7. The use as claimed in one or more of claims 1 to 6, in which R³ is an alkyl or alkenyl group having 2 to 12 carbon atoms.

8. The use as claimed in one or more of claims 1 to 7, in which R⁴ corresponds to a radical of the formula (4)

15



in which R⁶ is a radical of the formulae

20 -(B)-(O-A)_n-O-CO-R⁵ (2)

or

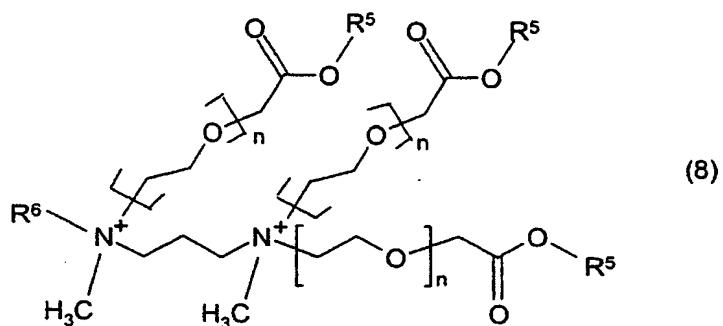
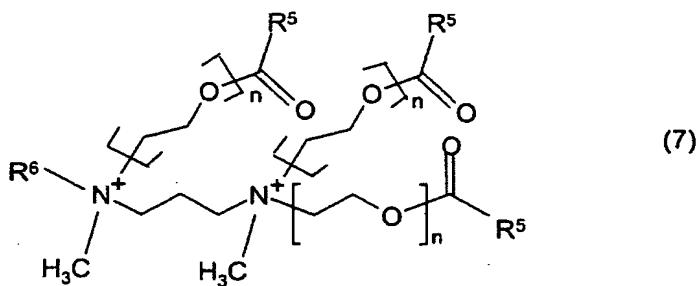
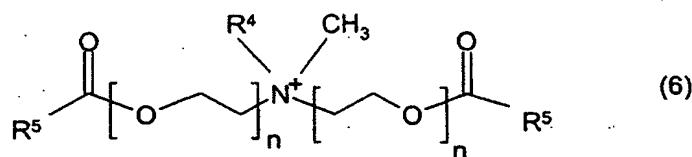
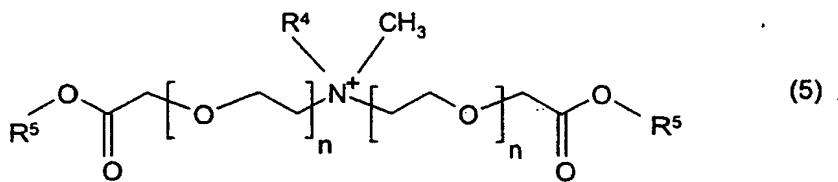
-(A-O)_n-(C)-CO-O-R⁵ (3)

25

or C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl and k is 2 or 3.

9. The use as claimed in one or more of claims 1 to 8, in which compounds of the formulae (5) to (8)

30

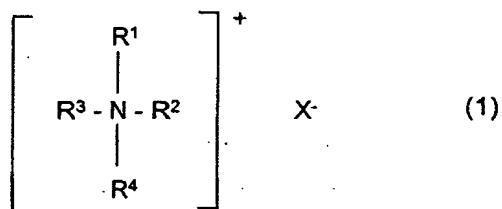


are used

5 10. A compound of the formula (1), but where those compounds in
 which R^4 does not contain a heteroatom and R^1 and R^2 simultaneously
 have the meaning given in formula (2) are excluded.

1. The use of compounds of the formula 1

5



in which

 R^1, R^2 , is a radical of the formula

10

 R^3 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl R^4 is an organic radical having 1 to 100 carbon atoms which optionally contains heteroatoms R^5 is C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl

n is a number from 1 to 20

A is a C₂- to C₄-alkylene group,C is a C₁- to C₆-alkylene group and

20 X is an anion

as corrosion inhibitors.

2. The use as claimed in claim 1, in which A is an ethylene or propylene group.

25

3. The use as claimed in claim 1 and/or 2, in which C is a C₂- to C₄-alkylene group.

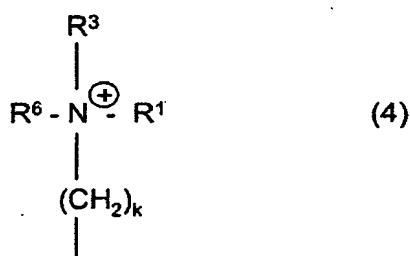
4. The use as claimed in one or more of claims 1 to 3, in which n is a

30 number between 2 and 6.

5. The use as claimed in one or more of claims 1 to 4, in which R^5 is an alkyl or alkenyl group having 2 to 24 carbon atoms.

6. The use as claimed in one or more of claims 1 to 5, in which R^3 is
5 an alkyl or alkenyl group having 2 to 12 carbon atoms.

7. The use as claimed in one or more of claims 1 to 6, in which R^4 corresponds to a radical of the formula (4)



10

in which R^6 is a radical of the formula

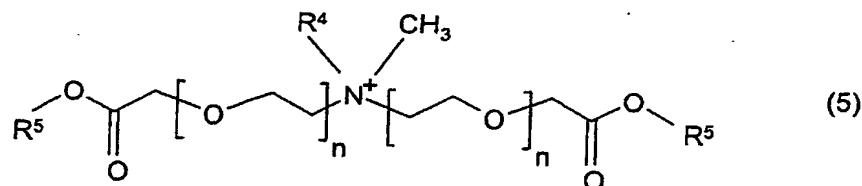


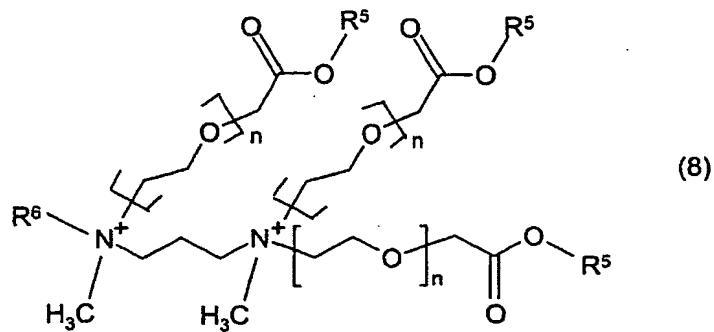
15

or C₁- to C₃₀-alkyl or C₂- to C₃₀-alkenyl and k is 2 or 3.

8. The use as claimed in one or more of claims 1 to 7, in which compounds of the formulae (5) or (8)

20





are used.

5 10. A compound of the formula (1), but where those compounds in which R^4 does not contain a heteroatom and R^1 and R^2 simultaneously have the meaning given in formula (2) are excluded.